<Division of Multidisciplinary Chemistry>Interdisciplinary Chemistry for Innovation

Division of Multidisciplinary Chemistry
– Interdisciplinary Chemistry for Innovation –

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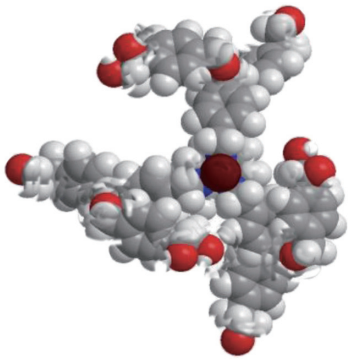
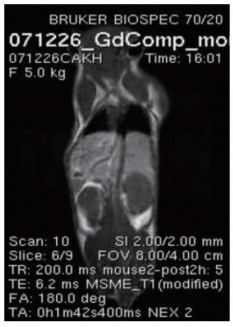
Scope of Research

Organic chemistry can contribute to the innovation through the design and synthesis of molecules those are valuable to human society. Our methodology possesses advantage in heteroatom chemistry, transition metal-catalyzed reactions, and asymmetric synthesis. As for the synthetic procedure, we take note to develop atom-economic as well as environment-benign reactions. We recognize the importance of the collaboration with various fields of technology of industry and academia. Recent examples of our projects include design, synthesis, and evaluation of aromatic compounds used in light-emitting field-effect transistors, sugar-fullerene linked compounds used in photodynamic therapy of cancers, and gadolinium complex of chiral dendrimers used in magnetic resonance imaging of cancers (shown in the figure).





KEYWORDS

Innovation
Organic Synthesis
Heteroatom Chemistry
Transition Metal Catalyst
Asymmetric Synthesis

Selected Publications

Kondo, T.; Kimura, Y.; Kanda, T.; Takagi, D.; Wada, K.; Toshimitsu, A., Simple and Practical Aerobic Oxidation of Alcohols Catalyzed by a (μ-Oxo)tetraruthenium Cluster, *Green Sus. Chem.*, (in press).

Kondo, T.; Niimi, M.; Yoshida, Y.; Wada, K.; Mitsudo, T.; Kimura, Y.; Toshimitsu, A., Rhodium-catalyzed Linear Codimerization and Cycloaddition of Ketenes with Alkynes, *Molecules*, **15,** 4189-4200 (2010).

Sakanoue, T.; Yahiro, M.; Adachi, C.; Takimiya, K.; Toshimitsu, A., Electrical Characteristics of Single-component Ambipolar Organic Field-effect Transistors and Effects of Air Exposure of Them, *J. Appl. Phys.*, **103,** [094509-1]-[094509-6] (2008).

Sakanoue, T.; Yahiro, M.; Adachi, C.; Uchiuzou, H.; Takahashi, T.; Toshimitsu, A., Ambipolar Light-emitting Organic Field-effect Transistors Using a Wide-band-gap Blue-emitting Small Molecule, *Appl. Phys. Lett.*, **90,** [171118-1]-[171118-3] (2007).

Okamoto, K.; Nishibayashi, Y.; Uemura, S.; Toshimitsu, A., Asymmetric Carboselenation of Olefins with Aromatic Compounds, *Angew. Chem. Int. Ed. Engl.*, **44,** 3588-3591 (2005).

One-pot Synthesis of Rhodanines from Ketenes and Isothiocyanates Using Rhodium Catalyst

Rhodanines are highly important heterocyclic compounds used in the medical inspection of copper in liver, the metal-free dye-sensitized solar cell, and so on. However, the synthetic methods reported so far are limited to the multistep reactions. We succeeded in one-pot synthesis of rhodanines from ketenes and isothiocyanates using rhodium calalyst. Thus, by the reaction of phenylethylketene (2.5 mmol) and ethylisothiocyante (1 mmol) in demethylacetamide as solvent in the presence of $[RhCl(cod)]_2$ (0.0025 mmol) and dppb (0.005 mmol) at 80°C for 12 h, the rhodanine bearing phenyl and ethyl groups are preduced in 99% yield (Figure 1).

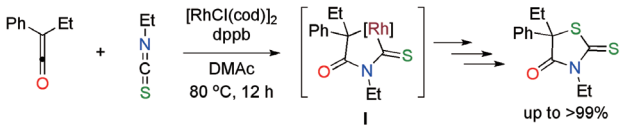
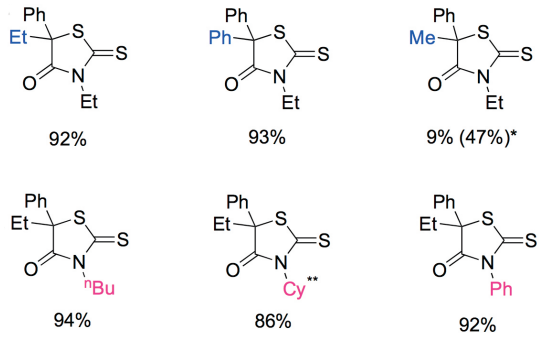


Figure 1. Synthesis of Rhodanin Derivatives.

It should be noted that one sulphur atom incorporated in the ring derives from second molecule of isothiocyanate with the elimination of isonitrile. The initial step of this reaction is expected to be the formation of rhodacyclic intermediate such as (**1**). Coordination of another isothiocyanate, followed by insertion of the C=S group into (**1**), dissociation of an isonitrile, and reductive elimination would afford the corresponding rhodanine.

Typical examples are summarized in Figure 2.



*Isothiocyanate was used in excess. **Cyclohexyl

Figure 2. Synthesis of Various Rhodanins.

Simple and Practical Aerobic Oxidation of Alcohols Catalyzed by Rhodium Cluster

The selective oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones, respectively, is a ubiquitous and pivotal reaction in organic synthesis and the chemical industry. Such oxidation reactions have been performed traditionally using stoichiometric amount of inorganic oxidants, such as CrO_3, $KMnO_4$, MnO_2, and SeO_2. However, these oxidation methods have serious drawbacks, such as their cost and the production of environmentally hazardous/toxic byproducts. From both economic and environmental viewpoints, there is an urgent demand for greener, more atom-efficient methods that use O_2 and *air* as readily available terminal and ideal oxidants, and produce only H_2O as a byproduct.

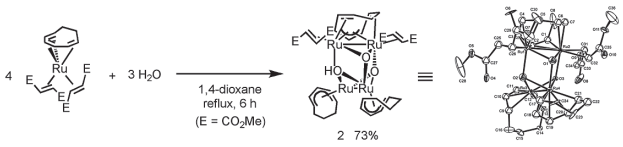


Figure 3. Synthesis of Catalyst.

We have found that the (μ-oxo)tetraruthenium cluster (**2**), prepared by the method shown in Figure 3, efficiently catalyzes a simple, practical, and selective oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones, respectively, under 1 atm of O_2 or air. For example, in the presence of **2** (0.005 mmol), benzyl alcohol (1 mmol) was smoothly oxidized in *N,N*-dimethylacetamide (DMA) at 80°C for 20 h under 1 atm of O_2 (balloon) to give benzaldehyde in 95% yield (Figure 4).

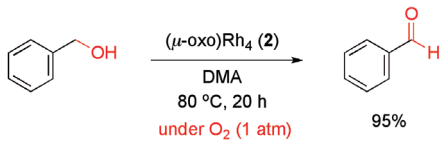


Figure 4. Oxidation of Alcohols.

Neither benzoic acid nor acetal of benzaldehyde was obtained at all. In the case of secondary alcohol, it was necessary to carry out the reaction at 130°C. At this condition, benzophenone was obtained quantitatively by the aerobic oxidation of diphenylmethanol.

After the reactions, **2** was recovered in 20% yield by simple column chromatography. In addition, mononuclear Ru(η^6-cot)(η^2-dmfm)$_2$, which is the starting material for the synthesis of **2**, showed no catalytic activity in either the absence or presence of a small amount of H_2O. These results strongly suggest that tetraruthenium cluster (**2**) acts as an active catalytic species throughout the reaction.